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H01L 21/027**(21)Application number : **2001-341740**(71)Applicant : **JSR CORP**(22)Date of filing : **07.11.2001**(72)Inventor : **KONNO KEIJI
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(30)Priority

Priority number : **2000339981** Priority date : **08.11.2000** Priority country : **JP****(54) COMPOSITION FOR RESIST LOWER LAYER FILM, RESIST LOWER LAYER FILM AND METHOD FOR MANUFACTURING THE SAME****(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a composition for a resist lower layer film having preferable gas permeability, excellent adhesiveness with a resist film and excellent durability against a developer for the development of the resist film and to provide the resist lower layer film and a method of manufacturing the film.

SOLUTION: The composition for a resist lower layer film contains a film forming component consisting of a hydrolyzed product and/or condensed product of a specified silane compound and contains a heat volatile substance which is gasified by heating. When the composition is heated, the film forming component is hardened while the heat volatile substance is gasified to form a porous silica film. The heat volatile substance preferably has 200 to 450°C boiling point or decomposition temperature. The density of the resist lower film to be formed is preferably 0.7 to 1.8 g/cm³. The resist lower film is formed by heating the thin film of the above composition at a temperature equal to or higher than the boiling point or the decomposition temperature of the heat volatile substance.

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CLAIMS

[Claim(s)]

[Claim 1] The constituent for resist lower layer film characterized by to form the porosity silica film by coming to contain the film formation component which consists of hydrolyzate of the silane compound (A) expressed with the following general formula (A), and/or its condensate, and the heating vaporization nature matter which it is heated and is gasified, the heating vaporization nature matter's gasifying with heating while a film formation component hardens, and forming a hole.

[Formula 1]

一般式 (A) $R^1_a Si(OR^2)_{4-a}$

(R1 shows a hydrogen atom, a fluorine atom, or a univalent organic radical, R2 shows a univalent organic radical, and a expresses the integer of 0-3.)

[Claim 2] The silane compound concerning a film formation component is a constituent for resist lower layer film according to claim 1 characterized by being the silane compound whose a is 0 or 1 in a general formula (A).

[Claim 3] The heating vaporization nature matter is a constituent for resist lower layer film according to claim 1 or 2 characterized by being the matter the boiling point or whose decomposition temperature is 200-450 degrees C.

[Claim 4] The constituent for resist lower layer film according to claim 3 characterized by being at least one sort chosen from the compound which has the aliphatic series polyether compound and naphthoquinonediazide structure where the heating vaporization nature matter consists of polyalkylene oxide which has Pori (meta) acrylate and the ether group content repeat unit of carbon numbers 2-12.

[Claim 5] The constituent for resist lower layer film according to claim 1 to 4 characterized by containing further the acid generating compound which generates an acid with either [at least] the exposure of ultraviolet radiation, or heating.

[Claim 6] it hardens by heating the thin film formed with the constituent for resist lower layer film according to claim 1 to 5, and forms -- having -- a consistency -- 0.7 - 1.8 g/cm³ it is -- resist lower layer film characterized by consisting of porosity silica film.

[Claim 7] The manufacture approach of the resist lower layer film characterized by forming the porosity silica film by making the heating vaporization nature matter gasify and forming a hole while stiffening a film formation component by forming a thin film with the constituent for resist lower layer film according to claim 1 to 5, and heating this thin film to the boiling point of the heating vaporization nature matter contained in the constituent concerned, or the temperature more than decomposition temperature.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In case this invention forms a resist pattern in the base for processing, it relates to the constituent for resist lower layer film, the resist lower layer film, and its manufacture approach for forming the lower layer film used as the substrate.

[0002]

[Description of the Prior Art] In the pattern formation in manufacture of the component for semi-conductors etc., necessary micro processing is performed to the base for processing which consists of an organic material or an inorganic material by the pattern replica method which applies a lithography technique, a resist development process, and an etching technique. However, an error (deviation) may arise in the dimension of a pattern under the effect of the standing wave of the light which it becomes difficult to imprint the pattern of an optical mask on the resist film in an exposure process at accuracy, for example, is form into the resist film in the micro-processing process over the base for processing as high integration of the semiconductor device in the circuit board etc. progresses. And in order to mitigate the effect of such a standing wave, forming an antireflection film between the resist film and the front face of the base for processing is known.

[0003] Although a resist pattern is used as a mask at the process which, on the other hand, processes the base for processing with which silicon oxide, an inorganic interlayer insulation film, etc. were formed, it becomes difficult to perform necessary micro processing, without being unable to obtain sufficient mask engine performance for the resist film concerned, since it is required to make thickness of the resist film small with detailed-izing of a pattern, consequently giving a damage to the base for processing. Then, a resist pattern is imprinted for an oxide film and the lower layer film for interlayer insulation film processing to be formed on the oxide film of the base which is an object for processing, and the process which carries out dry etching of an oxide film or the interlayer insulation film is performed, using the lower layer film for processing concerned as a mask. It is the film with which the lower layer film for processing is formed here at the lower layer of what serves as a lower layer antireflection film, or an antireflection film. since [appropriate] it is alike and the etch rate of the resist film and the lower layer film for processing approximates in this process, forming the mask layer for processing the lower layer film itself for processing concerned between the resist film and the lower layer film for processing is proposed. The approach of specifically forming the multilayer structure which carries out the laminating of the lower layer film for processing, the mask for lower layer film processing, and the resist film to this order, and becomes on an oxide film is proposed.

[0004] Although the thing to the surface resist film is the wet process which generally used the developer, the process which forms a pattern in each class in the multilayer structure of such a configuration In order for the thing to the layer below the lower layer film for processing to be the dry process which used etching gas and to etch selectively the mask for lower layer film processing, and the lower layer film for processing Usually, in order to form the pattern of the mask for lower layer film processing, an alkyl fluorine system type of gas is used, in order to form the pattern of the lower layer film for processing, an etching gas kind is changed and ashing using oxygen gas is performed.

[0005] However, in the process which carries out ashing of this lower layer film for processing, it is difficult to destroy the mask for lower layer film processing concerned, and to form a detailed pattern in accuracy. When the cause was studied, it became clear that it was a reason for the consistency of the mask for lower layer film processing concerned to be high, and not to have sufficient gas permeability. Moreover, the thing for which a good resist pattern without skirt length etc. is formed as other properties to the mask for lower

layer film processing, Although it is required that it has mask engine performance sufficient as a mask for processing for excelling in adhesion with a resist and the lower layer film for processing and that it should have the preservation stability excellent in the solution which forms the mask for lower layer film processing concerned in a list, the ingredient which fills these all is not known.

[0006]

[Problem(s) to be Solved by the Invention] This invention is made based on the above situations, and the object is to offer the constituent for resist lower layer film which was excellent in adhesion with the resist film, and was excellent in the resistance over the developer with which the development of the resist film is presented while having good gas permeability. Other objects of this invention are to offer the resist lower layer film which was excellent in adhesion with the resist film, and was excellent in the resistance over the developer with which the development of the resist film is presented while having good gas permeability. The object of further others of this invention is to offer the approach of manufacturing the resist lower layer film which was excellent in adhesion with the resist film, and was excellent in the resistance over the developer with which the development of the resist film is presented while having good gas permeability.

[0007]

[Means for Solving the Problem] The constituent for resist lower layer film of this invention is characterized by to form the porosity silica film by coming to contain the film formation component which consists of hydrolyzate of the silane compound (A) expressed with the following general formula (A), and/or its condensate, and the heating vaporization nature matter which it is heated and is gasified, the heating vaporization nature matter's gasifying with heating, while a film formation component hardens, and forming a hole.

[0008]

[Formula 2]

一般式 (A) $R^1_a S i (OR^2)_{4-a}$

(R1 shows a hydrogen atom, a fluorine atom, or a univalent organic radical, R2 shows a univalent organic radical, and a expresses the integer of 0-3.)

[0009] As for the silane compound concerning a film formation component, in the above-mentioned constituent for resist lower layer film, it is desirable in a general formula (A) that it is the silane compound whose a is 0 or 1.

[0010] Moreover, as for the heating vaporization nature matter, it is desirable that it is the matter the boiling point or whose decomposition temperature is 200-450 degrees C, and, as for this heating vaporization nature matter, it is desirable that it is at least one sort chosen from the compound which has the aliphatic series polyether compound and naphthoquinonediazide structure which consist of polyalkylene oxide which has Pori (meta) acrylate and the ether group content repeat unit of carbon numbers 2-12.

[0011] As for the above-mentioned constituent for resist lower layer film, it is desirable to contain further the acid generating compound which generates an acid with either [at least] the exposure of ultraviolet radiation or heating.

[0012] the resist lower layer film of this invention is hardened by heating the thin film formed with the above-mentioned constituent for resist lower layer film, and is formed -- having -- a consistency -- 0.7 - 1.8 g/cm³ it is -- it is characterized by consisting of porosity silica film.

[0013] By forming a thin film with the above-mentioned constituent for resist lower layer film, and heating this thin film to the boiling point of the heating vaporization nature matter contained in the constituent concerned, or the temperature more than decomposition temperature, the manufacture approach of the resist lower layer film of this invention is characterized by forming the porosity silica film by making the heating vaporization nature matter gasify and forming a hole while it stiffens a film formation component.

[0014]

[Function] Although the above-mentioned constituent for resist lower layer film is used for formation of the substrate layer of the resist film formed in the base for processing Since the constituent concerned contains the heating vaporization nature matter with the film formation component which consists of that to which hydrolysis and partial condensation of the silane compound were carried out, When a film formation component is hardened by heating, as a result of the heating vaporization nature matter's gasifying and vaporizing, the porosity silica film which has the comparatively low consistency in which a large number or a countless hole was formed is formed, and the resist lower layer film which has moderate gas permeability after all is formed. Therefore, this resist lower layer film can attain necessary vapor etching certainly and easily to the lower layer lower layer film for processing, when etching gas fully penetrates.

[0015] Moreover, the above-mentioned constituent for resist lower layer film has high adhesion with a resist, though it is porosity, since it is what a film formation component becomes from specific hydrolyzate and/or a specific condensate with a silane compound, and it has resistance big enough to the oxygen gas for ashing for removing a resist developer and a resist, the resist lower layer film with which a resist pattern with high repeatability is formed in the resist film can be formed, and the outstanding preservation stability is acquired.

[0016]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail. The constituent for resist lower layer film of this invention comes fundamentally to contain the film formation component which consists of specific matter, and the heating vaporization nature matter which gasifies and vaporizes with heating.

[0017] In this invention, the hydrolyzate of the silane compound (A) expressed with the above-mentioned general formula (A) and/or its condensate are used as a film formation component which is a subject component of the constituent for resist lower layer film.

[0018] It sets to the general formula (A) concerning a silane compound (A), and is R1. It is a hydrogen atom, a fluorine atom, or a univalent organic radical, and is R2. Although it is a univalent organic radical, as an example of a univalent organic radical, an aryl group, an alkyl group, a glycidyl group, etc. can be mentioned here. And as an example of an alkyl group, the alkyl group of the carbon numbers 1-5, such as a methyl group, an ethyl group, a propyl group, and butyl, can be mentioned. Even if these alkyl groups are straight chains-like, they may be the alkyl group fluoride by which you could branch and a part or all of a hydrogen atom was further permuted by the fluorine atom. Moreover, as an example of an aryl group, a phenyl group, a naphthyl group, a tosyl group, an ethyl phenyl group, a chlorophenyl radical, a BUROMO phenyl group, a fluoro phenyl group, etc. can be mentioned.

[0019] As an example of a silane compound (A) expressed with a general formula (A), following silane compound (1) - (5) can be mentioned.

Silane compound (1)

It sets to a general formula (A) and a is 1 and R1. A hydrogen atom or a fluorine atom, and R2 As an example of silane ***** which is the alkyl group or phenyl group of carbon numbers 1-5 For example, trimethoxysilane, triethoxysilane, tree n-propoxysilane, Tree iso-propoxysilane, tree n-butoxysilane, tree sec-butoxysilane, Tree tert-butoxysilane, triphenoxysilane, fluoro trimethoxysilane, Fluoro triethoxysilane, fluoro tree n-propoxysilane, Fluoro tree iso-propoxysilane, fluoro tree n-butoxysilane, fluoro tree sec-butoxysilane, fluoro tree tert-butoxysilane, fluoro triphenoxysilane, etc. can be mentioned.

[0020] Silane compound (2)

It sets to a general formula (A) and a is 0 and R2. As an example of silane ***** which is the alkyl group or phenyl group of carbon numbers 1-5, a tetramethoxy silane, a tetra-ethoxy silane, tetra--n-propoxysilane, tetra--iso-propoxysilane, a tetra--n-butoxy run, tetra--sec-butoxysilane, tetra--tert-butoxysilane, a tetra-phenoxy silane, etc. can be mentioned, for example.

[0021] Silane compound (3)

It sets to a general formula (A) and a is 1 and R1. The alkyl group or permutation alkyl group of carbon numbers 1-5, It is a vinyl group or a phenyl group, and is R2. As an example of silane ***** which is the alkyl group or phenyl group of carbon numbers 1-5 For example, methyl trimethoxysilane, methyl triethoxysilane, methyl tree n-propoxysilane, Methyl tree iso-propoxysilane, methyl tree n-butoxysilane, Methyl tree sec-butoxysilane, methyl tree tert-butoxysilane, Methyl triphenoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, Ethyl tree n-propoxysilane, ethyl tree iso-propoxysilane, Ethyl tree n-butoxysilane, ethyl tree sec-butoxysilane, Ethyl tree tert-butoxysilane, ethyl triphenoxysilane, Vinyltrimethoxysilane, vinyltriethoxysilane, vinyl tree n-propoxysilane, Vinyl tree iso-propoxysilane, vinyl tree n-butoxysilane, Vinyl tree sec-butoxysilane, vinyl tree tert-butoxysilane, Vinyl triphenoxysilane, n-propyltrimethoxysilane, n-propyl triethoxysilane, n-propyl tree n-propoxysilane, n-propyl tree iso-propoxysilane, n-propyl tree n-butoxysilane, n-propyl tree sec-butoxysilane, n-propyl tree tert-butoxysilane, n-propyl triphenoxysilane, iso-propyltrimethoxysilane, iso-propyl triethoxysilane, iso-propyl tree n-propoxysilane, iso-propyl tree iso-propoxysilane, iso-propyl tree n-butoxysilane, iso-propyl tree sec-butoxysilane, iso-propyl tree tert-butoxysilane, iso-propyl triphenoxysilane, [0022] n-butyltrimethoxysilane, n-butyltriethoxysilane, n-butyl tree n-propoxysilane, n-butyl tree iso-propoxysilane, n-butyl tree n-butoxysilane, n-butyl tree sec-butoxysilane, n-butyl tree tert-butoxysilane, n-butyl triphenoxysilane, sec-butyltrimethoxysilane, sec-butyl-iso-triethoxysilane, sec-butyl-tree n-propoxysilane, sec-butyl-tree iso-propoxysilane, sec-butyl-tree n-butoxysilane, sec-butyl-tree sec-butoxysilane, sec-butyl-tree tert-butoxysilane, sec-butyl-triphenoxysilane,

tert-butyltrimethoxysilane, tert-epoxybutyltriethoxysilane, tert-butyl tree n-propoxysilane, tert-butyl tree iso-propoxysilane, tert-butyl tree n-butoxysilane, tert-butyl tree sec-butoxysilane, tert-butyl tree tert-butoxysilane, tert-butyl triphenoxysilane, phenyltrimethoxysilane, Phenyltriethoxysilane, phenyl tree n-propoxysilane, Phenyl tree iso-propoxysilane, phenyl tree n-butoxysilane, Phenyl tree sec-butoxysilane, phenyl tree tert-butoxysilane, Phenyl triphenoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, gamma-truffe ROROPURO pill trimethoxysilane, gamma-truffe ROROPURO pill triethoxysilane, etc. can be mentioned.

[0023] Silane compound (4)

It sets to a general formula (A) and a is 2 and R1. The alkyl group or permutation alkyl group of carbon numbers 1-5, It is a vinyl group or a phenyl group, and is R2. As an example of silane ***** which is the alkyl group or phenyl group of carbon numbers 1-5 For example, dimethyldimethoxysilane, dimethyl diethoxysilane, dimethyl-G n-propoxysilane, Dimethyl-G iso-propoxysilane, dimethyl-G n-butoxysilane, Dimethyl-G sec-butoxysilane, dimethyl-G tert-butoxysilane, A JIMECHIRUJI phenoxy silane, diethyldimethoxysilane, diethyldiethoxysilane, Diethyl-G n-propoxysilane, diethyl-G iso-propoxysilane, Diethyl-G n-butoxysilane, diethyl-G sec-butoxysilane, Diethyl-G tert-butoxysilane, a JIECHIRUJI phenoxy silane, G n-propyl dimethoxysilane, di-n-propyl diethoxysilane, G n-propyl-G n-propoxysilane, G n-propyl-G iso-propoxysilane, G n-propyl-G n-butoxysilane, G n-propyl-G sec-butoxysilane, G n-propyl-G tert-butoxysilane, a G n-propyl-G phenoxy silane, G iso-propyl dimethoxysilane, G iso-propyl diethoxysilane, G iso-propyl-G n-propoxysilane, G iso-propyl-G iso-propoxysilane, G iso-propyl-G n-butoxysilane, G iso-propyl-G sec-butoxysilane, G iso-propyl-G tert-butoxysilane, a G iso-propyl-G phenoxy silane, [0024] Di-n-butyl dimethoxysilane, di-n-butyl diethoxysilane, Di-n-butyl-G n-propoxysilane, di-n-butyl-G iso-propoxysilane, Di-n-butyl-G n-butoxysilane, di-n-butyl-G sec-butoxysilane, Di-n-butyl-G tert-butoxysilane, a di-n-butyl-G phenoxy silane, G sec-butyl dimethoxysilane, G sec-butyl diethoxysilane, G sec-butyl-G n-propoxysilane, G sec-butyl-G iso-propoxysilane, G sec-butyl-G n-butoxysilane, G sec-butyl-G sec-butoxysilane, G sec-butyl-G tert-butoxysilane, a G sec-butyl-G phenoxy silane, G tert-butyl dimethoxysilane, G tert-butyl diethoxysilane, G tert-butyl-G n-propoxysilane, G tert-butyl-G iso-propoxysilane, G tert-butyl-G n-butoxysilane, G tert-butyl-G sec-butoxysilane, G tert-butyl-G tert-butoxysilane, a G tert-butyl-G phenoxy silane, Diphenyldimethoxysilane, a diphenyl-G ethoxy silane, diphenyl-G n-propoxysilane, Diphenyl-G iso-propoxysilane, diphenyl-G n-butoxysilane, Diphenyl-G sec-butoxysilane, diphenyl-G tert-butoxysilane, A diphenyl JIFENOKI gardenia fruit run, divinyl dimethoxysilane, JI gamma-aminopropyl dimethoxysilane, JI gamma-aminopropyl diethoxysilane, JI gamma-glycidoxypropyldimethoxysilane, JI gamma-glycidoxy propyl diethoxysilane, JI gamma-truffe ROROPURO pill dimethoxysilane, JI gamma-truffe ROROPURO pill diethoxysilane, etc. can be mentioned.

[0025] Silane compound (5)

It sets to a general formula (A) and a is 3 and R1. The alkyl group or permutation alkyl group of carbon numbers 1-5, It is a vinyl group or a phenyl group, and is R2. As an example of silane ***** which is the alkyl group or phenyl group of carbon numbers 1-5 For example, trimethyl monochrome methoxysilane, a trimethyl monochrome ethoxy silane, Trimethyl monochrome-n-propoxysilane, trimethyl monochrome-iso-propoxysilane, A trimethyl monochrome-n-butoxy gardenia fruit run, a trimethyl monochrome-sec-butoxy gardenia fruit run, A trimethyl monochrome-tert-butoxy gardenia fruit run, a trimethyl monochrome phenoxy silane, Triethyl mono-methoxysilane, a triethyl mono-ethoxy silane, triethyl mono--n-propoxysilane, Triethyl mono--iso-propoxysilane, triethyl mono--n-butoxysilane, Triethyl mono--sec-butoxysilane, triethyl mono--tert-butoxysilane, A triethyl mono-phenoxy silane, tree n-propyl mono--n-propyl methoxysilane, A tree n-propyl mono--n-ethoxy silane, tree n-propyl mono--n-propoxysilane, Tree iso-propyl mono--n-propoxysilane, tree n-propyl mono--n-butoxysilane, Tree n-propyl mono--tert-butoxysilane, tree n-propyl mono--sec-butoxysilane, A tree n-propyl mono-phenoxy silane, tree iso-propyl mono-methoxysilane, Tree iso-propyl mono--n-propoxysilane, tree iso-propyl mono--iso-propoxysilane, Tree iso-propyl mono--n-butoxysilane, tree iso-propyl mono--sec-butoxysilane, Tree iso-propyl mono--tert-butoxysilane, a tree iso-propyl mono-phenoxy silane, Triphenyl mono-methoxysilane, a triphenyl mono-ethoxy silane, Triphenyl mono--n-propoxysilane, triphenyl mono--iso-propoxysilane, Triphenyl mono--n-butoxysilane, triphenyl mono--sec-butoxysilane, triphenyl mono--tert-butoxysilane, a triphenyl mono-phenoxy silane, etc. can be mentioned.

[0026] Things desirable as a silane compound (2) among more than are a tetramethoxy silane, a tetra-ethoxy silane, tetra--n-propoxysilane, tetra--iso-propoxysilane, and a tetra-phenoxy silane. A thing desirable as a

silane compound (3) Methyl trimetoxysilane, Methyl triethoxysilane, methyl tree n-propoxysilane, methyl tree iso-propoxysilane, Ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimetoxysilane, Vinyltriethoxysilane, iso-propyltrimethoxysilane, iso-propyl triethoxysilane, n-butyltrimethoxysilane, They are n-butyltriethoxysilane, iso-butyltrimethoxysilane, iso-epoxybutyltriethoxysilane, tert-butyltrimethoxysilane, tert-epoxybutyltriethoxysilane, phenyltrimethoxysilane, and phenyltriethoxysilane. Things desirable as a silane compound (4) are dimethyldimethoxysilane, dimethyl diethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, diphenyldimethoxysilane, and diphenyl diethoxysilane. Things desirable as a silane compound (5) are trimethyl monochrome methoxysilane, a trimethyl monochrome ethoxy silane, triethyl mono-methoxysilane, a triethyl mono-ethoxy silane, triphenyl mono-methoxysilane, and a triphenyl mono-ethoxy silane.

[0027] The above silane compound (A) may use together not only one sort but two sorts or more. And in using the dialkoxysilane the mono-alkoxysilane whose value of a in a general formula (A) is the silane compound (A) of 2, or whose value of a is the silane compound (A) of 3, in order to obtain the constituent which has required hardenability, it is desirable to use together any one sort of the tetra-alkoxysilane whose value of a is the silane compound (A) of 0-1, and trialkoxysilane, or two sorts or more. In this case, let the rate of the mono-alkoxysilane or the dialkoxysilane which can be set be the range of 1 - 50 mass % of the whole silane compound (A). Moreover, when using two or more sorts of silane compounds (A) of an except in this case, especially that relative rate is not limited.

[0028] In the above-mentioned silane compound (A), hydrolysis and/or in order to carry out condensation, a catalyst is used. As this catalyst, metal chelate compound, an organic acid, an inorganic acid, an organic base, an inorganic base, etc. can be mentioned.

[0029] As metal chelate compound used as a catalyst For example, TORIETOKISHI monochrome (acetylacetonato) titanium, tree n-propoxy monochrome (acetylacetonato) titanium, Tree iso-propoxy monochrome (acetylacetonato) titanium, Tree n-butoxy monochrome (acetylacetonato) titanium, tree sec-butoxy monochrome (acetylacetonato) titanium, Tree tert-butoxy monochrome (acetylacetonato) titanium, Diethoxy screw (acetylacetonato) titanium, G n-propoxy screw (acetylacetonato) titanium, G iso-propoxy screw (acetylacetonato) titanium, G n-butoxy screw (acetylacetonato) titanium, G sec-butoxy screw (acetylacetonato) titanium, G tert-butoxy screw (acetylacetonato) titanium, Mono-ethoxy tris (acetylacetonato) titanium, Monod n-propoxy tris (acetylacetonato) titanium, Monod iso-propoxy tris (acetylacetonato) titanium, Monod n-butoxy tris (acetylacetonato) titanium, Monod sec-butoxy tris (acetylacetonato) titanium, Monod tert-butoxy tris (acetylacetonato) titanium, tetrakis (acetylacetonato) titanium, [0030] TORIETOKISHI monochrome (ethyl acetoacetate) titanium, tree n-propoxy monochrome (ethyl acetoacetate) titanium, Tree iso-propoxy monochrome (ethyl acetoacetate) titanium, Tree n-butoxy monochrome (ethyl acetoacetate) titanium, tree sec-butoxy monochrome (ethyl acetoacetate) titanium, Tree tert-butoxy monochrome (ethyl acetoacetate) titanium, Diethoxy screw (ethyl acetoacetate) titanium, G n-propoxy screw (ethyl acetoacetate) titanium, G iso-propoxy screw (ethyl acetoacetate) titanium, G n-butoxy screw (ethyl acetoacetate) titanium, G sec-butoxy screw (ethyl acetoacetate) titanium, G tert-butoxy screw (ethyl acetoacetate) titanium, Mono-ethoxy tris (ethyl acetoacetate) titanium, Monod n-propoxy tris (ethyl acetoacetate) titanium, Monod iso-propoxy tris (ethyl acetoacetate) titanium, Monod n-butoxy tris (ethyl acetoacetate) titanium, Monod sec-butoxy tris (ethyl acetoacetate) titanium, Monod tert-butoxy tris (ethyl acetoacetate) titanium, Tetrakis (ethyl acetoacetate) titanium, monochrome (acetylacetonato) tris (ethyl acetoacetate) titanium, Titanium chelate compound, such as screw (acetylacetonato) screw (ethyl acetoacetate) titanium and tris (acetylacetonato) monochrome (ethyl acetoacetate) titanium;

[0031] A TORIETOKISHI monochrome (acetylacetonato) zirconium, a tree n-propoxy monochrome (acetylacetonato) zirconium, A tree iso-propoxy monochrome (acetylacetonato) zirconium, A tree n-butoxy monochrome (acetylacetonato) zirconium, A tree sec-butoxy monochrome (acetylacetonato) zirconium, A tree tert-butoxy monochrome (acetylacetonato) zirconium, A diethoxy screw (acetylacetonato) zirconium, a G n-propoxy screw (acetylacetonato) zirconium, A G iso-propoxy screw (acetylacetonato) zirconium, A G n-butoxy screw (acetylacetonato) zirconium, a G sec-butoxy screw (acetylacetonato) zirconium, A G tert-butoxy screw (acetylacetonato) zirconium, A mono-ethoxy tris (acetylacetonato) zirconium, a Monod n-propoxy tris (acetylacetonato) zirconium, A Monod iso-propoxy tris (acetylacetonato) zirconium, A Monod n-butoxy tris (acetylacetonato) zirconium, A Monod sec-butoxy tris (acetylacetonato) zirconium, a Monod tert-butoxy tris (acetylacetonato) zirconium, a tetrakis (acetylacetonato) zirconium, [0032] A TORIETOKISHI monochrome (ethyl acetoacetate) zirconium, a tree n-propoxy monochrome (ethyl acetoacetate) zirconium, A tree iso-propoxy monochrome (ethyl acetoacetate) zirconium, A tree n-butoxy monochrome (ethyl acetoacetate) zirconium, A tree sec-butoxy monochrome (ethyl acetoacetate) zirconium,

A tree tert-butoxy monochrome (ethyl acetoacetate) zirconium, A diethoxy screw (ethyl acetoacetate) zirconium, a G n-propoxy screw (ethyl acetoacetate) zirconium, A G iso-propoxy screw (ethyl acetoacetate) zirconium, A G n-butoxy screw (ethyl acetoacetate) zirconium, A G sec-butoxy screw (ethyl acetoacetate) zirconium, A G tert-butoxy screw (ethyl acetoacetate) zirconium, A mono-ethoxy tris (ethyl acetoacetate) zirconium, a Monod n-propoxy tris (ethyl acetoacetate) zirconium, A Monod iso-propoxy tris (ethyl acetoacetate) zirconium, A Monod n-butoxy tris (ethyl acetoacetate) zirconium, A Monod sec-butoxy tris (ethyl acetoacetate) zirconium, A Monod tert-butoxy tris (ethyl acetoacetate) zirconium, A tetrakis (ethyl acetoacetate) zirconium, a monochrome (acetylacetonato) tris (ethyl acetoacetate) zirconium, A screw (acetylacetonato) screw (ethyl acetoacetate) zirconium, Zirconium chelate compounds, such as a tris (acetylacetonato) monochrome (ethyl acetoacetate) zirconium; Tris (acetylacetonato) aluminum, Aluminum chelate compounds, such as tris (ethyl acetoacetate) aluminum; others can be mentioned.

[0033] As an organic acid, for example An acetic acid, a propionic acid, butanoic acid, pentanoic acid, A hexanoic acid, oenanthic acid, an octanoic acid, nonoic acid, a decanoic acid, oxalic acid, A maleic acid, a methylmalonic acid, an adipic acid, a sebacic acid, a gallic acid, Butanoic acid, a merit acid, an arachidonic acid, a MIKIMI acid, 2-ethylhexanoic acid, Oleic acid, stearin acid, linolic acid, the Reno Laing acid, a salicylic acid, A benzoic acid, p-aminobenzoic acid, p-toluenesulfonic acid, benzenesulfonic acid, monochloroacetic acid, dichloroacetic acid, a trichloroacetic acid, trifluoroacetic acid, a formic acid, a malonic acid, a sulfonic acid, a phthalic acid, a fumaric acid, a citric acid, a tartaric acid, etc. can be mentioned. As an inorganic acid, a hydrochloric acid, a nitric acid, a sulfuric acid, fluoric acid, a phosphoric acid, etc. can be mentioned, for example.

[0034] As an organic base, a pyridine, a pyrrole, a piperazine, a pyrrolidine, a piperidine, picoline, a trimethylamine, triethylamine, monoethanolamine, diethanolamine, dimethyl monoethanolamine, monomethyl diethanolamine, triethanolamine, a diaza BISHIKU roke run, a diazabicyclo nonane, diazabicycloundecen, tetramethylammonium hydroxide, etc. can be mentioned, for example. As an inorganic base, ammonia, a sodium hydroxide, a potassium hydroxide, a barium hydroxide, a calcium hydroxide, etc. can be mentioned, for example.

[0035] Among these catalysts, desirable things are metal chelate compound, an organic acid, and an inorganic acid, and can mention titanium chelate compound and an organic acid as a more desirable thing. These catalysts can use together one sort or two sorts or more.

[0036] the amount of the catalyst used -- the 100 mass sections (it converts as a full hydrolysis condensate) of a silane compound (A) -- receiving -- usually -- 0.001 - 10 mass section -- it is the range of 0.01 - 10 mass section preferably.

[0037] In order to perform hydrolysis and partial condensation of a silane compound (A), it is desirable to add 0.3-2.5-mol water especially 0.25-3 mols per one mol of the whole silane compound alkoxy groups, and the paint film formed with the constituent for resist lower layer film obtained in this case becomes a homogeneous high thing, and the constituent concerned becomes what has certainly high preservation stability. What is necessary is just to specifically add water intermittently or continuously in the organic solvent in which the silane compound (A) was dissolved. You may add beforehand in an organic solvent and the water added may be made to dissolve or distribute a catalyst. 0-100 degrees C of reaction temperature of this hydrolysis and partial condensation are usually 15-80 degrees C preferably.

[0038] In this invention, the heating vaporization nature matter which is blended with the above film formation component and constitutes the constituent for resist lower layer film is a compound which the boiling point or decomposition temperature is 200-450 degrees C, and gasifies and vaporizes when heated by such temperature. The boiling point or decomposition temperature shows the temperature under 1 atmospheric pressure here.

[0039] As for the heating vaporization nature matter, it is desirable that it is the organic compound of the hydrocarbon system containing association or the polar group of ether linkage, an ester bond, amide association, carbonate association, urea association, sulfide association, sulfonyl association, amino association, carbonyl association, hydroxyl, a thiol group, the amino group, etc. Since there is an inclination for a paint film low compatibility with a film formation component and transparent not to be obtained, and for a big hole to be formed into the film, the hydrocarbon compound which does not contain these association or radicals has a possibility that the regist-patterning engine performance may fall. As an example of the heating vaporization nature matter, an ultrafine particle etc. can be mentioned to the combination of the compound which has a polyalkylene oxide compound, the compound which has naphthoquinonediazide structure, the compound which has sugar chain structure, a vinyl amide system polymer, an acrylate (meta) system polymer, an oleophilic compound, and a dispersant, and a list, for

example.

[0040] When the heating vaporization nature matter is [the boiling point or decomposition temperature] a less than 200-degree C compound In order to gasify it before a film formation component hardens the matter concerned, a necessary hole is not formed in the film, but when it is the matter with which the boiling point or decomposition temperature exceeds 450 degrees C on the other hand Since hardening of a film formation component advances substantially before it gasifies, it is difficult for a paint film to form a hole, therefore in any case, it is difficult to obtain the resist lower layer film which has necessary gas permeability.

[0041] although the blending ratio of coal of the heating vaporization nature matter in the constituent for resist lower layer film changes with the class of film formation component, classes of the heating vaporization nature matter concerned, etc. -- usually -- the 100 mass sections of a film formation component -- receiving -- 0.1 - 80 mass section -- it is the range of 1 - 50 mass section preferably. It is difficult for the resist lower layer film obtained as the blending ratio of coal of the heating vaporization nature matter is excessive to become what has small reinforcement, and to, form the good porosity silica film made into the object on the other hand, when too little.

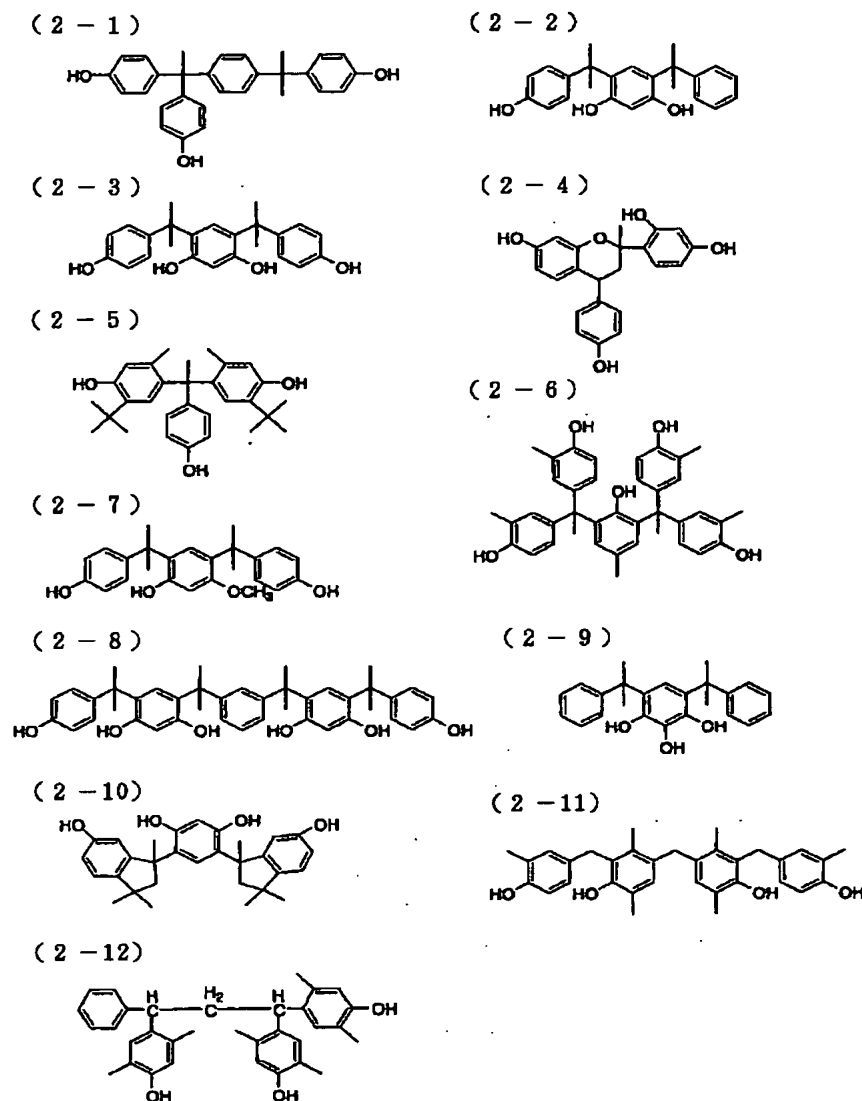
[0042] Below, the matter useful as heating vaporization nature matter is explained.

(1) As polyalkylene oxide structure in the compound of ***** which has polyalkylene oxide structure, polyethylene oxide structure, polypropylene oxide structure, polytetramethylene oxide structure, polybutylene oxide structure, etc. can be mentioned. As a concrete example of a compound, for example Polyoxyethylene alkyl ether, Polyoxyethylene alkyl phenyl ether, the polyoxyethylene sterol ether, A polyoxyethylene lanolin derivative, the ethylene oxide derivative of an alkylphenol formalin condensate, Ether mold compounds, such as a polyoxyethylene polyoxypropylene block copolymer and polyoxyethylene polyoxypropylene alkyl ether, Polyoxyethylene glycerine fatty acid ester, polyoxyethylene sorbitan fatty acid ester, Ether ester mold compounds, such as polyoxyethylene sorbitol fatty acid ester and a polyoxyethylene fatty-acid-alkanolamide sulfate, Polyethylene glycol fatty acid ester, ethylene glycol fatty acid ester, Ether ester mold compounds, such as a fatty-acid monoglyceride, polyglyceryl fatty acid ester, a sorbitan fatty acid ester, propylene glycol fatty acid ester, and sucrose fatty acid ester, etc. can be mentioned.

[0043] (2) As a compound which has the compound naphthoquinonediazide structure of having naphthoquinonediazide structure, the naphthoquinone -1 of the compound which has phenol structure, and a 2-diazido-5-sulfonate can be mentioned. As a compound which has phenol structure, the following compound (2-1) - (2-12) others can be mentioned to a phenol, methyl phenol, dimethylphenol, a trimethyl phenol, a tetramethyl phenol, a pentamethyl phenol, resorcinol, a catechol, a hydroquinone, bisphenol A, a dihydroxy benzophenone, dihydroxy diphenylsulfone, dihydroxy diphenyl ether, dihydroxy diphenylmethane, a resorcinol allene compound, a calyx allene compound, and a list.

[0044]

[Formula 3]

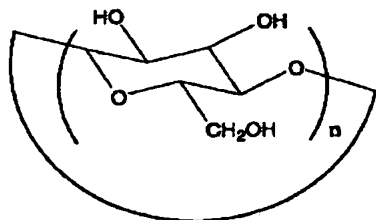


[0045] (3) As a compound which has the compound sugar chain structure of having sugar chain structure, cyclodextrin, cane-sugar ester, an oligosaccharide, a glucose, a fructose, mannite, starch sugar, D-sorbitol, a dextran, xanthan gum, curdlan, a pullulan, a cycloamylose, isomerized sugar, maltitol, cellulose acetate, a cellulose, a carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylcellulose, methyl cellulose, ethyl hydroxyethyl cellulose, a chitin, chitosan, etc. can be mentioned. Cyclodextrin is expressed with the following formula (1) and n in a formula is 6 (alpha-cyclodextrin), 7 (beta-cyclodextrin), or 8 (gamma-cyclodextrin).

[0046]

[Formula 4]

式 (1)



[0047] The compound which has the sugar chain structure where it is used as heating vaporization nature matter has that desirable to which a part or all of the hydroxyl group or the amino group denaturalized. As chemistry denaturation of a hydroxyl group, denaturation including etherification, esterification, trialkylsilyl

association, and a urethane bond can be mentioned. Moreover, as chemistry denaturation of the amino group, installation of amide association, an urea bond, and imide association can be mentioned.

[0048] Among the compounds which have the above sugar chain structure, the hole formed in a paint film becomes the thing of a minor diameter, moreover is the point which can control an aperture, and cyclodextrin's is desirable as heating vaporization nature matter. When chemistry denaturation is carried out, urethane--ization[trialkylsilyl denaturation or]-denaturalizing is desirable, and it is desirable that especially trimethylsilyl denaturation is carried out.

[0049] What is necessary is just to usually permute 5 - 100% which has sugar chain structure of the hydroxyl group of a compound that what is necessary is just to make trimethylsilylation agents, such as trimethylchlorosilane and a trimethylsilyl acetamide, react to the compound which has sugar chain structure, in order to denaturalize the compound which has sugar chain structure by the trimethylsilyl radical. What is necessary is just to usually permute 5 - 100% which has sugar chain structure of the hydroxyl group of a compound that what is necessary is just to make urethane-ized agents, such as phenyl isocyanate and hexyl isocyanate, react to the compound which has sugar chain structure, in order to urethane--ization-denaturalize the compound which has sugar chain structure.

[0050] (4) As a vinyl amide system polymer vinyl amide polymer, they are Pori (N-vinyl acetamide) and Pori (N-vinyl pyrrolidone, Pori (2-methyl-2-oxazoline), Pori (N and N-dimethyl acrylamide), etc. can be mentioned.).

[0051] (5) (meta) As an acrylate system polymer (meta) acrylate system polymer, the polymer or copolymer of a radical polymerization nature monomer by acrylic ester (meta), such as a methyl acrylate (meta), an ethyl acrylate (meta), butyl acrylate (meta), acrylic-acid (meta) benzyl, acrylic-acid (meta) tetrahydrofurfuryl, metaglycidyl acrylate (meta), hydroxyethyl (meta) acrylate, acrylamide (meta), and hydroxypropyl (meta) acrylate, can be mentioned.

[0052] (6) Although there is much what does not fully have compatibility to a film formation component only with a lipophilic compound, since sufficient compatibility is acquired by combining with a dispersant, an oleophilic compound, a dispersant oleophilic compound, and a dispersant can be used as heating vaporization nature matter. As an oleophilic compound, polycarboxylic acid ester, such as JIDESHIRU phthalate, di-undecyl phthalate, didodecyl phthalate, di-tridecyl phthalate, tris (2-ethylhexyl) trimellitate, tridecyl trimellitate, tridodecyl trimellitate, tetrabutyl pyromellitate, tetra-hexyl trimellitate, tetra-octyl pyromellitate, screw (2-ethylhexyl) dodecane dioate, and bis-decyl dodecandioate, and others can be mentioned, for example. As a dispersant combined with these oleophilic compounds, higher alcohol, such as an octanol, lauryl alcohol, decyl alcohol, and undecyl alcohol, can be mentioned. The higher alcohol as a dispersant is used in the range of an amount 0.1 to 10 times both in quality and in quantity to an oleophilic compound.

[0053] (7) Particle size is a polymer particle 100nm or less, for example, particle size is controlled by regulating conditions, such as a class of emulsifier, emulsifier concentration, and agitating speed, in the usual emulsion polymerization, and as the example, it has some which were prepared using the cross-linking monomer for particle-size control while an acrylate (meta) compound is used for an ultrafine particle ultrafine particle as a monomer.

[0054] When the above-mentioned film formation component and the heating vaporization nature matter are dissolved or distributed by the proper solvent, the constituent for resist lower layer film of this invention is prepared. Although it is not limited here especially if it is the organic solvent used for this kind of application as a solvent, the propylene glycol monoethyl ether, propylene glycol monomethyl ether, the propylene glycol monopropyl ether, etc. are used especially preferably.

[0055] An acid generator can be added in the constituent for resist lower layer film of this invention. According to the constituent containing an acid generator, an acid is generated according to an operation of heat or light in the resist lower layer film. Since the repeatability of a good mask pattern and the rectangle nature of a cross-section profile can form a high resist pattern in formation of a resist pattern by this, it is desirable.

[0056] As an acid generator, a latency heat acid generator or a latency photo-oxide generating agent can be mentioned. 50-450 degrees C of latency heat acid generators are usually the compound which generates an acid by heating at 200-350 degrees C preferably, and onium salts, such as sulfonium salt, a benzothiazolium salt, ammonium salt, and phosphonium salt, are used.

[0057] As an example of the sulfonium salt used as a latency heat acid generator 4-aceto phenyl dimethyl sulfonium Hexafluoroantimonate, 4-acetoxyphenyl dimethyl sulfonium Hexafluoroarsenate, Dimethyl-4-(benzyloxy carbonyloxy) phenyl sulfonium Hexafluoroantimonate, Dimethyl-4-(benzoyloxy) phenyl

sulfonium Hexafluoroantimonate, Dimethyl-4-(benzoyloxy) phenyl sulfonium Hexafluoroarsenate, Dimethyl-3-chloro-4-acetoxyphenyl sulfonium Alkyl sulfonium salt, such as hexafluoroantimonate; benzyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, Benzyl-4-hydroxy phenylmethyl sulfonium Hexafluorophosphate, 4-acetoxyphenyl benzyl methyl sulfonium Hexafluoroantimonate, Benzyl-4-methoxy phenylmethyl sulfonium Hexafluoroantimonate, Benzyl-2-methyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, Benzyl-3-chloro-4-hydroxy phenylmethyl sulfonium Hexafluoroarsenate, Benzyl sulfonium salt, such as 4-methoxybenzyl-4-hydroxy phenylmethyl sulfonium hexafluorophosphate, benzoin tosylate, and 2-nitrobenzyl tosylate;

[0058] Dibenzyl-4-hydroxyphenyl sulfonium Hexafluoroantimonate, Dibenzyl-4-hydroxyphenyl sulfonium Hexafluorophosphate, 4-acetoxyphenyl dibenzyl sulfonium Hexafluoroantimonate, Dibenzyl-4-methoxyphenyl sulfonium Hexafluoroantimonate, Dibenzyl-3-chloro-4-hydroxyphenyl sulfonium Hexafluoroarsenate, Dibenzyl -3 - Methyl-4-hydroxy-5-tert-buthylphenyl sulfonium Hexafluoroantimonate, Benzyl-4-methoxybenzyl-4-hydroxyphenyl sulfonium Dibenzyl sulfonium salt, such as hexafluorophosphate; p-chloro benzyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, p-nitrobenzyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, p-chloro benzyl-4-hydroxy phenylmethyl sulfonium Hexafluorophosphate, p-nitrobenzyl-3-methyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, 3, 5-dichloro benzyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, o - Chloro benzyl-3-chloro-4-hydroxy phenylmethyl sulfonium Permutation benzyl sulfonium salt, such as hexafluoroantimonate, can be mentioned.

[0059] Moreover, as an example of a benzothia ZONIUMU salt, it is 3-benzyl benzothiazolium. Hexafluoroantimonate, 3-benzyl benzothiazolium Hexafluorophosphate, 3-benzyl benzothiazolium Tetrafluoroborate, 3-(p-methoxybenzyl) benzothiazolium Hexafluoroantimonate, 3-benzyl-2-methylthio benzothiazolium Hexafluoroantimonate, 3-benzyl-5-chlorobenzo thiazolium Benzyl benzothiazolium salts, such as hexafluoroantimonate, can be mentioned. Furthermore, 2, 4, 4, and 6-tetrabromo cyclohexa JIENON can be illustrated as heat acid generators other than the above.

[0060] The above inside, 4-acetoxyphenyl dimethyl sulfonium Hexafluoroarsenate, benzyl-4-hydroxy phenylmethyl sulfonium Hexafluoroantimonate, 4-acetoxyphenyl benzyl methyl sulfonium hexafluoroantimonate, dibenzyl-4-hydroxyphenyl sulfonium Hexafluoroantimonate, 4-acetoxyphenyl benzyl sulfonium Hexafluoroantimonate, 3-benzyl benzothiazolium hexafluoroantimonate, etc. are used preferably. As these commercial items, it is SAN-AID. SI-L85, this SI-L110, this SI-L145, this SI-L150, this SI-L160 (product made from 3 Japanese Federation of Chemical Industry Workers' Unions Industry), etc. can be mentioned. these compounds are independent -- it is -- two or more sorts can be used together.

[0061] A latency photo-oxide generating agent is usually a compound which generates an acid by the ultraviolet radiation exposure of the energy of 10-50mJ preferably one to 100 mJ. As a latency photo-oxide generating agent, for example Diphenyliodonium trifluoromethane sulfonate, Diphenyliodonium pyrene sulfonate, diphenyliodonium dodecylbenzene sulfonate, Diphenyliodonium nona fluoro n-butane sulfonate, screw (4-tert-buthylphenyl) iodonium trifluoromethane sulfonate, Screw (4-tert-buthylphenyl) iodonium dodecylbenzene sulfonate, Screw (4-tert-buthylphenyl) iodonium naphthalene sulfonate, Screw (4-tert-buthylphenyl) iodonium hexafluoroantimonate, Screw (4-tert-buthylphenyl) iodonium nona fluoro n-butane sulfonate, Triphenylsulfonium trifluoromethane sulfonate, triphenylsulfonium hexafluoroantimonate, Triphenylsulfonium naphthalene sulfonate, triphenylsulfonium nona fluoro-n-butane sulfonate, Diphenyl (4-methylphenyl) sulfonium trifluoromethane sulfonate, Diphenyl (4-methoxyphenyl) sulfonium trifluoromethane sulfonate, Benzene methyl sulfonium toluenesulfonate, (Hydroxyphenyl) Cyclohexyl methyl (2-oxocyclohexyl) sulfonium trifluoromethane sulfonate, dicyclohexyl (2-oxocyclohexyl) sulfonium trifluoromethane sulfonate, [0062] Dimethyl (2-oxocyclohexyl) sulfonium trifluoromethane sulfonate, Diphenyliodonium hexafluoroantimonate, triphenylsulfonium camphor sulfonate, Benzyl methyl sulfonium toluenesulfonate, (4-hydroxyphenyl) 1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 1-NAFUCHIRUJIECHIRU sulfonium trifluoromethane sulfonate, 4-cyano-1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 4-nitro-1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 4-methyl-1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 4-cyano-1-naphthyl-diethyl sulfonium trifluoromethane sulfonate, 4-nitro-1-NAFUCHIRUJIECHIRU sulfonium trifluoromethane sulfonate, 4-methyl-1-NAFUCHIRUJIECHIRU sulfonium trifluoromethane sulfonate, 4-hydroxy-1-NAFUCHIRUJIMECHIRU sulfonium trifluoromethane sulfonate, 4-hydroxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-methoxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-ethoxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-methoxy methoxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-ethoxy methoxy-1-

naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-(1-methoxyethoxy)-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-(2-methoxyethoxy)-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-methoxycarbonyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4 - Ethoxy cull BUNIRU oxy--1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-n-propoxycarbonyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, [0063] 4-iso-propoxycarbonyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-n-BUTOKI carbonyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-tert-butoxycarbonyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-(2-tetrahydrofuranyl oxy-)-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-(2-tetrahydropyranyloxy)-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, 4-benzyloxy-1-naphthyl tetrahydro CHIOFENIUMU trifluoromethane sulfonate, Onium salt system photo-oxide generating agents, such as 1-(naphthyl aceto methyl) tetrahydro CHIOFENIUMU trifluoromethane sulfonate; Phenyl-screw (TORIKURORO methyl)-s-triazine, Halogen content compound system photo-oxide generating agents, such as methoxyphenyl-screw (TORIKURORO methyl)-s-triazine and naphthyl-screw (TORIKURORO methyl)-s-triazine; [0064] 1, 2-naphthoquinonediazide-4-sulfonyl chloride, 1, 2-naphthoquinonediazide-5-sulfonyl chloride, Diazoketone compound system photo-oxide generating agent; 4-tris phenacyl sulfones, such as a 1 of 2, 3, 4, and 4'-tetra-benzophenone, and 2-naphthoquinonediazide-4-sulfonate or 1, and 2-naphthoquinonediazide-5-sulfonate, Sulfonic-acid compound system photo-oxide generating agents, such as a mesityl phenacyl sulfone and screw (phenyl sulfonyl) methane; Benzoin tosylate, The tris trifluoromethane sulfonate of pyrogallol, nitrobenzyl -9, 10-diethoxy anthracene-2-sulfonate, The trifluoromethane sulfonyl bicyclo [2, 2, 1] hept-5-en -2, 3-JIKARUBO diimide, Sulfonic-acid compound system photo-oxide generating agents, such as N-hydroxysuccinimide trifluoromethane sulfonate, 1, and 8-naphthalene dicarboxylic acid imide trifluoromethane sulfonate, can be mentioned. These are independent, there are, can be and can use two or more sorts together.

[0065] In any [of a latency heat acid generator and a latency photo-oxide generating agent] case, the above acid generator is usually 1 - 30 mass section to the film formation component 100 mass section (it converts as a full hydrolysis condensate).

[0066] In the constituent for resist lower layer film of this invention, auxiliary components, such as a colloid silica, a colloid alumina, and a surfactant, may be added further. The mean particle diameter to which the colloid silica distributed the silicic acid anhydride of a high grade in the organic solvent is 5-30 micrometers, preferably, mean particle diameter is 10-20 micrometers, and solid content concentration is about 10 - 40 % of the weight. As such a colloid silica, a methanol silica sol, an isopropanol silica sol (above, Nissan Chemical Industries, Ltd. make), Oscar (made in [Industrial] formation [Catalyst]), etc. can be mentioned, for example. as a colloid alumina -- alumina sol 520 -- said -- 100 -- said -- 200 (above, Nissan Chemical Industries, Ltd. make), an alumina clear sol, and alumina sol 10 -- said -- 132 (above, Kawaken Fine Chemicals Co., Ltd. make) etc. can be mentioned. As a surface active agent, the Nonion system surface active agent, an anion system surface active agent, a cation system surface active agent, an amphoteric surface active agent, a silicone system surface active agent, a polyalkylene oxide system surface active agent, and a fluorine-containing surface active agent can be mentioned, for example.

[0067] The constituent for resist lower layer film of this invention is used for formation of the substrate layer of the resist film formed in the base for processing. The solution of the constituent concerned is specifically applied to the front face which should form the resist lower layer film, a paint film is formed, and it hardens by being heated after this paint film is dried. And by controlling whenever [in this hardening / stoving temperature] to proper temperature, make the heating vaporization nature matter concerned gasify, it is made to vaporize, and the resist lower layer film which consists of porosity silica film with which a large number or a countless hole was formed by this is formed. The refractive index of this resist lower layer film is usually the thing of 1.2-1.6.

[0068] The front face in which the resist lower layer film of this invention is formed will not be especially limited, if the resist film is formed on the resist lower layer film concerned. With a concrete example, the resist lower layer film concerned is formed in the front face of the lower layer film for processing formed on the oxide film of the base for processing, and the resist lower layer film concerned forms the film used as a mask for lower layer film processing in this case.

[0069] Although the temperature which heats a paint film needs to be temperature higher than the boiling point or decomposition temperature of the heating vaporization nature matter contained in the constituent in the formation process of the above resist lower layer film, therefore it considers as the temperature of 200-

450 degrees C or more Proper temperature is selected by the conditions of the class of the class of film formation component actually used, the class of curing catalyst and a rate, and heating vaporization nature matter, the class of additive of comparatively others and a rate, and others. And the condition of the porosity in the resist lower layer film formed, the pitch diameter of the hole specifically formed, and extent of distribution should be controlled by adjusting whenever [this stoving temperature], and heating time. [0070] thus, the porosity silica film which constitutes the resist lower layer film formed -- the consistency -- for example, 0.7 - 1.8 g/cm³ it is -- things are desirable. By having the comparatively low consistency of such range, when it becomes that in which the resist lower layer film itself [concerned] has good gas permeability, therefore etching gas fully penetrates, necessary vapor etching can be attained certainly and easily to the lower layer film for processing currently formed as a lower layer of the resist lower layer film concerned.

[0071] Moreover, since the constituent for resist lower layer film of this invention is what a film formation component becomes from specific hydrolyzate and/or a specific condensate with a silane compound so that clearly from the example mentioned later, The resist lower layer film formed has high adhesion with a resist, though it is porosity. It has resistance big enough to the oxygen gas for ashing for removing a resist developer and a resist, the resist lower layer film with which a resist pattern with high repeatability is formed in the resist film can be formed, and, moreover, the outstanding preservation stability is acquired.

[0072]

[Example] Although the concrete example of this invention is explained hereafter, this invention is not limited to these examples.

[0073] After dissolving tetramethoxy silane 30.1g and methyl trimetoxysilane 2.6g of an example 1(1) silane compound (A) in propylene glycol monopropyl ether 154g of an organic solvent, it stirred by the three one motor and solution temperature was stabilized at 60 degrees C. After adding in this solution over 1 hour and making the water solution made to dissolve 0.12g of maleic acids of a catalyst in 15.7g of ion exchange water react to it at 60 degrees C after that for 4 hours, reaction mixture was cooled to the room temperature. And after removing 51g of solutions which contain a methanol from reaction mixture at the temperature of 50 degrees C by evaporation, propylene glycol monopropyl ether 51g was added, and film formation component liquid was obtained.

(2) In 50g of film formation component liquid obtained above (1), the weight average molecular weight which is triphenylsulfonium trifluoromethane sulfonate 0.09g which is a latency photo-oxide generating agent, and the heating vaporization nature matter whose decomposition temperature is 330 degrees C added poly tetrahydrofurfuryl methacrylate 1.20g of 7000, it fully stirred in it, this solution was further filtered in it with the filter whose aperture is 0.2 micrometers, and the constituent for resist lower layer film was obtained in it.

[0074] In 50g of film formation component liquid obtained like example 2 example 1, the weight average molecular weight which is triphenylsulfonium trifluoromethane sulfonate 0.09g which is a latency photo-oxide generating agent, and the heating vaporization nature matter whose decomposition temperature is 300 degrees C added polyethylene oxide 1.20g of 2000, it fully stirred in it, this solution was further filtered in it with the filter whose aperture is 0.2 micrometers, and the constituent for resist lower layer film was obtained in it.

[0075] Triphenylsulfonium trifluoromethane sulfonate 0.09g which is a latency photo-oxide generating agent at 50g of film formation component liquid obtained like example 3 example 1, 4- which is the heating vaporization nature matter whose decomposition temperature is 350 degrees C (Naphthoquinone -1 and 2-diazido-5-sulfonyl)-4' - (add 1-methyl (4-screw (naphthoquinone -1, 2-diazido-5-sulfonyl) -1, 1-diphenyl) methyl isopropylidene diphenyl 1.20g, and it fully stirs) Furthermore, this solution was filtered with the filter of 0.2-micrometer aperture, and the constituent for resist lower layer film was obtained.

[0076] In example of comparison 1 example 1, the constituent for resist lower layer film was obtained like the example 1 except having used the polystyrene whose decomposition temperature is 340 degrees C instead of poly tetrahydrofurfuryl methacrylate as heating vaporization nature matter.

[0077] In example of comparison 2 example 1, the constituent for resist lower layer film was obtained like the example 1 except having used the Pori alpha methyl styrene whose decomposition temperature is 70 degrees C instead of poly tetrahydrofurfuryl methacrylate as heating vaporization nature matter.

[0078] [Assessment of the constituent for resist lower layer film] The following item was evaluated about each of the constituent for resist lower layer film concerning the above examples 1-3 and examples 1-2 of a comparison of a case.

(1) A film consistency and preservation stability of the repeatability (4) alkali-resistance (5) oxygen ashing

resistance (6) solution of the adhesion (3) resist pattern of a refractive-index (2) resist [0079] The assessment approach of above-mentioned item (1) - (6) is as follows.

[Formation of a resist pattern] Using the constituent for resist lower layer film of a sample, the resist lower layer film was formed as follows, the resist film was formed further, and the resist pattern was formed. That is, thickness used the thing which is 300nm and which carried out the antireflection film as a base for processing by applying the charge of antireflection-film lumber "NFC B007" (product made from JIEI S R) by the spin coater, and making it dry for 1 minute on a 190-degree C hot plate on the surface of a silicon wafer. After applying the resist lower layer film constituent to the front face of the antireflection film of this base for processing by the spin coater and making it dry it for 1 minute on a 200-degree C hot plate, thickness formed the resist lower layer film which is 70nm by calcinating with a 300 more-degree C hot plate. The resist paint film whose thickness is 700nm by applying a positive type photoresist

"M20G" (product made from JIEI S R), and drying for 90 seconds at 130 degrees C is formed in the front face of this resist lower layer film. Furthermore, subsequently The KrF excimer laser (wavelength of 248nm) was irradiated with the energy of 25mJ(s) at the resist paint film through the optical mask made from a quartz which has 0.2-micrometer line - and - tooth-space pattern using the KrF excimer laser irradiation equipment by NIKON CORP. And after heat-treating a resist paint film for 90 seconds at 130 degrees C, the resist pattern was formed by carrying out a development for 30 seconds using the developer which consists of a tetramethylammonium hydroxide water solution of concentration 2.38 mass %.

[0080] (1) The film consistency and the refractive-index film consistency were measured by the X-ray scattering method. The value of a refractive index measured the refractive index of the location of 50 points using the optical refractometer "UV-1280SE" (product made from KLA-Tencor), and calculated the average.

[0081] (2) The adhesion resist pattern with a resist was observed with the scanning electron microscope, the case where the resist film had not exfoliated from the resist lower layer film was estimated as "fitness", and the case where it had exfoliated was estimated as the "defect."

[0082] (3) The repeatability resist pattern of a resist pattern was observed with the scanning electron microscope, and the film remainder of a resist did not arise in the part where laser was irradiated, but the case where "fitness" and a pattern were not reproduced in the case where the pattern of line - which is 0.2 micrometers of an optical mask, and - tooth space is reproduced faithfully was evaluated as a "defect."

[0083] (4) In the alkali-proof assessment development process, the thickness of the resist lower layer film before being immersed in a developer was compared with the thickness of the resist lower layer film after being immersed, and the case where it exceeded "fitness" and 2nm for the case where both difference is 2nm or less was estimated as the "defect."

[0084] (5) the oxygen-proof ashing nature resist lower layer film -- the barrel-type oxygen plasma -- ashing -- using equipment "--501" (the Yamato science company make), oxygen ashing processing was performed for 15 seconds by 300W, and the case where it exceeded "fitness" and 5nm for a being [the difference of the thickness of the resist lower layer film before processing and the thickness of the resist lower layer film after processing / 5nm or less] case was estimated as the "defect."

[0085] (6) The preservation stability of a solution was searched for as follows by making each of the constituent for resist lower layer film concerning the preservation stability examples 1-3 and the examples 1-2 of a comparison of a solution into a sample. The silicon wafer which used the spin coater, applied the constituent for resist lower layer film the condition for engine-speed 2000rpm and 20 seconds on the surface of the silicon wafer, and applied the constituent for resist lower layer film concerned using the hot plate held at the temperature of 190 degrees C after that was heat-treated for 2 minutes. About the obtained resist lower layer film, thickness was measured in the location of 50 points using the optical thickness gage (the product made from KLA-Tencor, UV-1280SE), and it asked for the average thickness. Moreover, using the constituent for resist lower layer film after saving for one month at the temperature of 40 degrees C, the resist lower layer film was formed like the above, thickness was measured, and it asked for the average thickness. And average thickness T0 of the paint film by the constituent for resist lower layer film before preservation A difference (T-T0) with the average thickness T of the paint film by the constituent for resist lower layer film after preservation is searched for. Average thickness T0 [(T-T0)/T0] was comparatively computed as thickness rate of change, and the case where it exceeded "fitness" and 10% for the case of the magnitude of the receiving difference where the value is 10% or less was estimated as the "defect."

[0086] The assessment result is as follows.

example 1(1) film consistency: -- the repeatability:fitness (4) alkali-resistance:fitness (thickness change width of face of 0.4nm) of the adhesion:fitness (3) resist pattern of 1.54 and refractive-index:1.34 (2) resist

(5) Oxygen ashing resistance : fitness (thickness change width of face of 2.5nm)

(6) Solution preservation stability : fitness (4.5% of thickness rate of increase)

[0087] example 2(1) film consistency: -- the repeatability:fitness (4) alkali-resistance:fitness (thickness change width of face of 0.5nm) of the adhesion:fitness (3) resist pattern of 1.60 and refractive-index:1.37 (2) resist

(5) Oxygen ashing resistance : fitness (thickness change width of face of 2.6nm)

(6) Solution preservation stability : fitness (4.3% of thickness rate of increase)

[0088] example 3(1) film consistency: -- the repeatability:fitness (4) alkali-resistance:fitness (thickness change width of face of 0.7nm) of the adhesion:fitness (3) resist pattern of 1.40 and refractive-index:1.32 (2) resist

(5) Oxygen ashing resistance : fitness (thickness change width of face of 2.9nm)

(6) Solution preservation stability : fitness (3.4% of thickness rate of increase)

[0089] example of comparison 1(1) film consistency: -- poor repeatability poor:(4) alkali-resistance: (thickness change width of face of 7nm) of the poor adhesion:(3) resist pattern of 1.85 and refractive-index:1.43 (2) resist

(5) Oxygen ashing resistance : fitness (thickness change width of face of 3.2nm)

(6) Solution preservation stability : defect (16.3% of thickness rate of increase)

[0090] example of comparison 2(1) film consistency: -- the repeatability poor:(4) alkali-resistance:fitness (thickness change width of face of 0.9nm) of the poor adhesion:(3) resist pattern of 2.0 and refractive-index:1.49 (2) resist

(5) Oxygen ashing resistance : defect (pattern destruction)

(6) Solution preservation stability : defect (16.3% of thickness rate of increase)

[0091]

[Effect of the Invention] Since the constituent for resist lower layer film of this invention contains the heating vaporization nature matter with the film formation component which consists of that to which hydrolysis and partial condensation of the silane compound were carried out, When a film formation component is hardened by heating, as a result of the heating vaporization nature matter's gasifying and vaporizing, the porosity silica film which has the comparatively low consistency in which a large number or a countless hole was formed is formed, and the resist lower layer film which has good gas permeability is formed. Therefore, this resist lower layer film can attain necessary vapor etching certainly and easily to the lower layer lower layer film for processing, when etching gas fully penetrates.

[0092] Moreover, the constituent for resist lower layer film of this invention has high adhesion with a resist, though it is porosity, since it is what a film formation component becomes from specific hydrolyzate and/or a specific condensate with a silane compound, and it has resistance big enough to the oxygen gas for ashing for removing a resist developer and a resist, the resist lower layer film with which a resist pattern with high repeatability is formed in the resist film can be formed, and the outstanding preservation stability is acquired.

[Translation done.]